A NEW TREATMENT PROCESS TO RECOVER MAGNETITE, ZINC AND LEAD FROM IRON AND STEELMAKING DUSTS AND SLUDGES

A. Delalio[1], Z. Bajger[2], P. Balaz[3], F. Castro[4]

INTRODUCTION

Steelmaking dusts are frequently classified as hazardous residues, due to their eco-toxicity characteristics. This derives mainly from the presence of heavy metals like zinc, lead and cadmium in their compositions, in forms that are easily leachable by water or slightly acidic or alkaline media. Following the most employed eco-toxicity standard tests, like DIN 38414-S4[1)] from Germany, and TCLP (Toxicity Characteristic Leaching Procedure)[2)] from the United States, steelmaking dusts present a high level of mobility of heavy metals, what is relevant for the evaluation of their environmental impact, when disposed in controlled landfills.

In the present project (contract number ERB IC 15CT97-0704), a new process is being developed to recover valuable metals and products from steelmaking dusts and sludges. Two different process routes are being evaluated, both from the technical and from the economic points of view. A pre-treatment stage, based on water leaching of the dusts, is, in both cases, studied, to remove alkalis present in the wastes.

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[1] Ecometal, s.r.l., Brescia, Italy
[2] Vítkovice, J.S.C., Ostrava-Vítkovice, Czech Republic
[3] Institute of Geotechnics, Kosice, Slovakia
[4] TecMinho, Guimarães, Portugal

The first procedure is based on the previous reduction of zinc and lead oxides to the metallic state, followed by its separation by vaporisation and physical means. Then, a magnetic separation step allows the recovery of magnetite. The remainder iron oxide phases, partially reduced, are then re-oxidised by controlled means to produce magnetite, that is again enriched by magnetic separation means.

The second procedure to be studied consists in a full oxidation of all the ironish phases to trivalent iron. Then, the controlled reduction is done until an important amount of magnetite may be easily separated by magnetic means. The final residue, containing concentrated amounts of lead and zinc is treated by hydrometallurgical means, employing ammonium chloride reagent.

CHARACTERISATION OF DUSTS

Twelve different dusts have been collected in companies from Slovakia, the Czech Republic and Portugal [3)].They are of the following types:

Basic Oxygen Furnace dusts – Sample 2 from Slovakia and sample 8 from the Czech Republic

Basic Oxygen Furnace sludges – Sample 1, from Slovakia, samples 3, 4 and 7, from the Czech Republic and sample 10 from Portugal.

Basic Oxygen Furnace muds – Samples 5 and 9 from the Czech Republic.

Ladle Furnace sludge – Sample 11 from Portugal.

Electric Arc Furnace dusts – Sample 6 from the Czech Republic and sample 12 from Portugal.

The following tables resume the characterisation that has been done, on a dried basis.

values in %

Sample	Zn	Pb	Fe	Mn	SiO_2	CaO	Cu	Cr
1	2.2	0.6	54	1.1	1.6	6.2	0.03	0.02
2	1.6	0.5	54	0.9	1.4	6.0	0.02	0.02
3	3.6	0.8	62	0.9	1.8	4.6	0.04	0.06
4	0.5	0.05	78	0.6	2.1	5.3	0.04	0.07
5	0.4	0.07	52	0.09	8.0	4.6	0.01	0.01
6	15.1	3.7	28	3.6	2.3	3.7	0.16	0.17
7	4.2	0.5	48	1.0	1.8	11.9	0.03	0.06
8	1.6	1.2	39	0.2	77.5	4.0	0.03	0.01
9	10.0	2.1	54	0.9	1.8	1.4	0.09	0.09
10	2.4	0.6	71	1.1	1.3	6.1	0.03	0.04
11	0.1	0.1	16	10.7	6.2	21.3	0.02	0.03
12	19.5	3.3	29	2.2	1.7	26.5	0.22	0.12

Table 1 – Chemical composition of the collected samples

Sample	Bulk Density ($g.cm^{-3}$)	Volume Magnetic Susceptib. ($x\ 10^3$) (SI units)	Specific Surface Area (m^2g^{-1})
1	3.34	162	21.6
2	3.54	451	7.9
3	4.84	145	11.0
4	5.75	448	0.75
5	3.88	104	5.3
6	4.79	310	3.7
7	3.84	87	13.2
8	3.63	87	10.4
9	4.98	326	7.1

Table 2 – Bulk density, volume magnetic susceptibility and specific surface area of some of the samples collected

Sample	< 0.04	0.04-0.063	0.063-0.100	0.100-0.125	0.125-0.250	0.250-0.500	0.500-1.000	> 1.00
1	52.1	4.8	6.0	2.3	5.8	3.9	20.1	5.0
2	72.7	8.3	3.6	1.5	5.3	6.9	1.8	---
3	17.6	2.3	3.3	0.5	4.9	7.0	16.4	48.0
4	2.4	0.7	1.0	0.5	2.1	4.0	9.4	79.9
5	62.8	8.0	9.6	3.5	7.6	4.8	3.7	---
6	85.9	3.2	3.9	1.0	1.9	1.9	2.2	---
7	45.4	7.8	10.5	1.6	3.3	4.2	14.3	12.9
8	22.6	6.8	6.8	3.8	7.8	4.4	7.0	40.8
9	41.1	9.7	6.9	1.5	3.0	2.2	11.7	23.9

grain size in mm, expressed in % of the total weight of the sample

Table 3 – Grain size distribution of some of the collected samples.

Specific surface area has been determined by the low temperature adsorption method in Gemini 2360 sorption apparatus, from Micrometrics. Volume magnetic susceptibility measurements have been achieved on the apparatus Kappabridge KLY-2/Geophysics Brno, Czech Republic, under the following conditions: intensity of magnetic field 920 Am^{-1}, homogeneity of field 0,2%, frequency 920 Hz.

In order to evaluate the dispersion of chemical composition data concerning electric arc furnace dusts, fifteen analysis have been done on samples from the same origin as sample 6. The average results, as well as the respective dispersion are presented bellow.

values in %

	Zn	Pb	FeO	Fe_2O_3
Average	15.1	3.7	4.2	34.7
Stand. Dev.	5.5	1.3	2.2	4.3

Table 4 – Dispersion of chemical analysis of EAF dusts (Sample 6).

The eco-toxicity characterisation of sample 12, by two standardised methods, gave the following results:

Test	DIN 38414-part 4	TCLP
pH	12.7	-----
Zn ($mg.l^{-1}$)	4	4
Pb ($mg.l^{-1}$)	330	320
SO_4^{2-} ($mg.l^{-1}$)	600	500

Table 5 – Results of the eco-toxicity tests applied to sample 12.

Results of both tests implies the classification of this residues as eco-toxic, due to high amount of dissolved lead.

By means of the simultaneous DTA/TGA characterisation of the dust's samples, done at the SDT 2960 equipment from TA Instruments available at the Laboratory of Metallurgy of the University of Minho, Guimarães, Portugal, several features can be highlighted:

- all the samples present a weight loss behaviour, at around 600 ºC;
- some samples (numbers 2, 4, 5 and 12) present also a first weight loss step, at around 400 ºC;
- both weight loss processes are endothermic ones;
- degrees of weight loss are highly variable from sample to sample, reaching, for samples 8 and 12, more than 25 % of the initial weight.

WATER WASHING BEHAVIOUR

Water washing behaviour has been evaluated for sample number 12. Cold distilled water at 25 ± 2 ºC was mixed with dried dust (at 110 ºC for 24 hours) and agitated with a glass stirrer, at a speed of 1100 r.p.m., during 24 hours. The extraction degree has been determined by chemical analysis of the water - by atomic absorpion spectrometry - and by the chemical analysis of the dusts - by X-ray fluorescence spectrometry - giving the following results:

values in % of extraction, except for pH

Liquid/solid ratio	pH	Na	K	S	Cl	Ca	Pb
20	12.7	> 99	92	38	97	5	28
10	12.8	> 99	91	36	97	8	25
5	12.9	> 99	92	14	97	< 2	21
3	12.8	> 99	92	14	96	< 2	16

Table 6 – Water leaching results, expressed in terms of pH of the solution after leaching, and of % of dissolution of elements present in dust number 12.

It is evident the high level of elimination of chlorides, what may be of relevance for the further treatment of dusts, in order to recover zinc, ferrites and lead, by pyro- or hydrometallurgical methods. The dissolution of an important part of the lead contained must be considered, taking into account the partial elimination of this heavy metal. However, this obliges to consider the elimination of this metal from the pre-treatment wastewaters, to respect environmental protection rules. The relatively high degree of dissolution of lead in water may be explained by the eventual presence of some lead chloride in the dusts, and also by the high alkalinity of the leachate.

To evaluate the possible effect of the sorption properties of iron compounds on the elimination of alkalies from the dusts, a pilot plant trial has been done, employing a iron rich dust sample (sample nº 11). This sample has an average of 2.7 % Na, 1.6 % K and 5.0 % Cl. The elimination of these elements by water washing lied in the range of 60 %, being far from the case of electric arc furnace dust washing, where the removal of alkalies as chlorides were almost complete. This difference of behaviour could be explained by the sorption in iron oxides contained in sample number 11. The Mossbauer study of this sample shows that around 30% of the iron is in a non-stoichiometric (substituted) magnetite $Fe_{3-x}M_xO_4$ (M are the substituents) and 70 % is present as a supermagnetic haematite α - Fe_2O_3.

TREATMENT OF WASHING SOLUTIONS

Removal of alkalies and chlorides from water washing solutions may be sucessfully done by evaporation. By this technique, a pre-concentration with model W/D-DS Italteco and dry-evaporation with model Dry-HP Italteco, allowed to evaluate an overall cost of around 45 Euro per cubic meter of solution.

For electric arc furnace dusts, the solubility of lead in washing waters obliges its removal. Precipitation with sulphuric acid or sodium sulphate allowed more than 90 % of elimination of lead, with a final lead content in waters in the order of 0,4 g/l.

SELECTIVE REDUCTION ROASTING OF DUSTS AND SLUDGES

For the rest of the project, but not yet finished at this moment, reduction of pre-treated dusts is to be done by carbon and gas mixtures of $CH_4 + CO_2$. The parameters to be determined are the material residence time, working temperature, carbon requirements and degree of recovery of volatile metals and iron oxides. For the moment, experiments with desulphurized coal as reduction agent, gave an efficiency of dry filtering for the metals cadmium, lead and zinc greater than 98,5 %. The reduction parameters will also be studied in order to partially reduce haematite to magnetite under controlled conditions.

MAGNETITE EXTRACTION

After the removal of metallic values from the dusts, the work will deal with the extraction of magnetite, from high iron content dusts. High Gradient Magnetic Separation (HGMS) will be employed for that purpose. Improvements of magnetic properties of the extracted magnetite will be tried by mechanical activation. The final magnetic product is going to be characterised for magnetic susceptibility.

CONDITIONING OF THE FINAL RESIDUE

The final residue from this treatment procedure will be conditioned by pelletizing, in order to produce a fluxing agent for the iron and steelmaking industry, or an inert residue to be dumped.

REFERENCES

1) Standard DIN 38414-S4, October 1984
2) U.S. E.P.A. SW 846, method 1311; Title 40-261.24 of the Code of Federal Regulation, in Federal Register, Vol. 51, number 114, June 13, 1986, pages 21648-21693.
3) DELALIO, A., BAIJGER, Z., BALAZ, P., F. CASTRO, MAGALHÃES, J., CURILLA, J. - *Characterisation and pre-treatment of steelmaking dusts in order to recover valuable products*, Acta Metallurgica Slovaca, 4, Special Issue, 1/1998, p. 55-59, 1998.